and

$$[C_1^-] = [NaOH] + Y[HML^-] + [H^+] \quad ...(9)$$

where

$$Y = 1 + 2\frac{[H^+]}{k_1}$$

$[HML_2^-]$ and $[C_1^-]$ were calculated using Eqs. 8 and 9 respectively. Concentration of the complex C is obtained by substracting $[C_1^-]$ from $[(CH_3)_2SnCl_2]$. K_1 was calculated according to Eq. 7 and the values are $3{\cdot}95\times10^{-5}$, $1{\cdot}35\times10^{-5}$ and $1{\cdot}01\times10^{-5}$ at *p*H 5·8, 5·9 and 6·0 respectively. The mean value of K_1 thus obtained is $2{\cdot}1\times10^{-5}$, which is in agreement with the value obtained earlier ($1{\cdot}606\times10^{-5}$).

In the *p*H range 6·4-9·0, both C_1^- and C_2^{2-} complexes exist as shown by the titration of system containing dimethyltin and malic acid in the ratio 1:1·25. Hence, it can be shown that[2,3]

$$[ML] = [(CH_3)_2SnCl_2] + x[HML^-] \quad ...(10)$$

and

$$[C_2^{2-}] = [NaOH] + Y[HML^-] + [H^+] - [(CH_3)_2SnCl_2] \quad ...(11)$$

$[HML^-]$ and $[C_2^{2-}]$ were calculated using Eqs. 10 and 11 respectively. $[C_1^-]$ was calculated by subtracting $[C_2^{2-}]$ from the total metal concentration. The mean value of K_2 thus obtained is $1{\cdot}98\times10^{-8}$ which is in close agreement with the value obtained earlier ($1{\cdot}55\times10^{-8}$).

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Stability Constants of Zirconyl Chelates with Substituted Azobenzenes

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Synthesis of 3-formyl-4-hydroxy-3′-nitroazobenzene (FH3′NB) and 3-formyl-4-hydroxy-4′-nitroazobenzene (FH4′NB) and determination of their proton-ligand stability constants and metal-ligand stability constants of their ZrO(II) complexes have been studied in 60% (w/w) ethanol-water solution at 28 ± 0·1° using Calvin-Bjerrum titration technique. It is found that FH3′NB has a stronger chelating tendency than FH4′NB but both of these are lesser chelating agents than 3-formyl-4-hydroxyazobenzene (FHB).

In this note we report the synthesis of 3-formyl-4-hydroxy-3′-nitroazobenzene (FH3′NB) and 3-formyl-4-hydroxy-4′-nitroazobenzene (FH4′NB) and the effect of nitro substituents on the stability of the chelates of these ligands with zirconium as determined by Calvin-Bjerrum potentiometric titration technique.

The ligands were synthesized from *m*-nitroaniline or *p*-nitroaniline and salicylaldehyde of AR grade according to a procedure similar to that reported earlier[1]. FH3′NB (Found: C, 57·25; H, 3·21; N, 15·42 reqd: C, 57·55; H, 3·32; N, 15·50%) and FH4′NB (Found: C, 57·34; H, 3·19; N, 15·38 reqd: C, 57·55; H, 3·32; N, 15·50%) are yellowish brown and reddish brown crystalline solids melting at 156° ± 1·5° and 195° ± 1·5° respectively. The molecular weights of FH3′NB and FH4′NB were found to be 271·9 and 272·5 respectively.

All the reagents used were of AR quality. Zirconyl chloride solution was prepared in doubly distilled water and standardized gravimetrically as mandelate.

A Systronic *p*H meter type 322 (accuracy ±0·05 units) was used for *p*H measurements. Titrations were carried out in 60% (w/w) ethanol-water mixture at 28° ± 0·1°. Adequate amount of potassium nitrate solution (1*M*) was added to keep the ionic strength constant at 0·2*M*. Corrections in *p*H values were made according to the method of Bates[2].

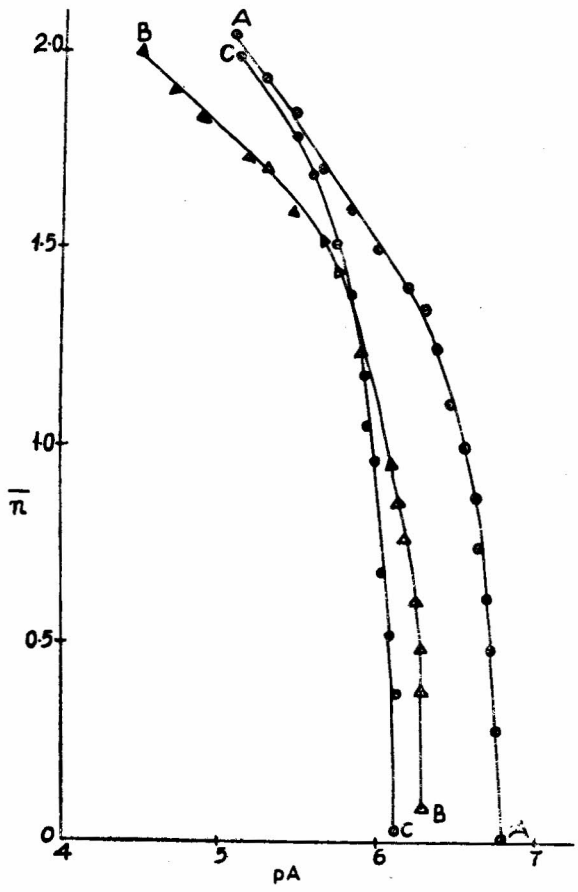

Fig. 1 — Formation curves of ZrO(II) complexes [A, ZrO(II) — FHB; B, ZrO(II) — FH3′NB; C, ZrO(II) — FH4′NB]

The following solutions were prepared (total volume 50 ml) and titrated against 0·2*M* sodium hydroxide solution in the absence and presence of metal ions respectively. (i) 1 ml of $4\times10^{-2}M$ $HClO_4$ +10 ml of 1·0*M* KNO_3, (ii) 1 ml of $4\times10^{-2}M$ $HClO_4$ +10 ml of 1·0*M* KNO_3+25 ml of $5\times10^{-3}M$ ligand solution, (iii) 1 ml of $4\times10^{-2}M$ $HClO_4$+10 ml of 1·0*M* KNO_3+25 ml of $5\times10^{-3}M$ ligand solution +5 ml of $5\times10^{-3}M$ metal salt solution. While titrating, the metal hydroxide got precipitated at *p*H 4·9, 5·6 and 5·7 in the case of FH4′NB, FH3′NB and 3-formyl-4-hydroxyazobenzene (FHB) respectively.

The acid dissociation constants were determined by the methods of Irving and Rossotti[3] and Bjerrum[4]. Formation curves for proton-ligand systems were drawn between $\bar{n}$H and *p*H. Calculations were also carried out using the equation

$$\log kH = \log \frac{\bar{n}H}{\bar{n}H-1} + pH$$

The *pk* values of FHB, FH3′NB and FH4′NB were found to be 7·9, 7·35 and 7·15 respectively.

The formation curves for metal-ligand system were drawn (Fig. 1) as plots between $\bar{n}$ and *p*A, the values of which were calculated by the method of Bjerrum and Calvin[5]. Log *k* values were taken directly from the formation curves (Table 1). The probable errors and the refined values are also given in Table 1. The values of overall changes of free energies ($\Delta F = -RT\ln k$) were also calculated. It is found that ZrO(II) forms 1:2 complexes in all the cases.

Introduction of a nitro group at 4′-position in 3-formyl-4-hydroxy-azobenzene increases the acidity of the compound more than the substitution at 3′-position as is evident from the *pk* values. Hence the ligands can be arranged in the order of their chelating tendencies as: FHB>FH3′NB>FH4′NB.

TABLE 1 — METAL-LIGAND STABILITY CONSTANTS AND FREE ENERGY VALUES FOR THE COMPLEXES

log k_1	log k_2	log β_2	ΔF (kcal/mole)
		ZrO(II)-FHB	
(a) 6·70	6·00	12·70±0·02	−17·50
(b)		12·90	
(c) 6·42	6·33	12·75	
(d) 6·82	6·13	12·95	
		ZrO(II)-FH3′NB	
(a) 6·25	5·66	11·91±0·03	−16·43
(b)		12·02	
(c) 6·27	5·50	11·77	
(d) 6·53	5·43	11·96	
		ZrO(II)-FH4′NB	
(a) 6·06	5·71	11·77±0·02	−16·24
(b)		11·88	
(c) 6·43	5·34	11·77	
(d) 6·10	5·56	11·66	

(a) Bjerrum-Calvin method. (b) Mid-points method. (c) Interpolation at different $\bar{n}$ values method. (d) Least-square method.

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Polarographic Study of Cd(II) & Pb(II) Chelates of Thiodiacetic Acid in Water & Aqueous DMF & DMSO

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Complexes with metal to ligand ratios, 1 : 1, 1 : 2 and 1 : 3 for Cd-thiodiacetic acid and 1 : 1 for Pb(II)-thiodiacetic acid are observed at *p*H 6·5 and 6 respectively. Values of stability constants β_1, β_2 and β_3 for Cd-TDAA system are 20, 60 and 245, 10, 55 and 175 and 8, 45 and 150 at 30°, 40° and 50°C and the values of β for Pb-TDAA system are 1103·4, 900 and 740 at 30, 40 and 50°C respectively.

IN view of earlier work[1,2] on the chelating behaviour of sulphur containing compounds, the chelates of thiodiacetic acid (TDAA) with Cd(II) and Pb(II) have now been investigated at d.m.e. in water and aq. DMF and aq. DMSO.

TDAA (Evans Chimetics) was of 98% purity and reagents like KNO_3, $3CdSO_4.8H_2O$ and gelatin were of AR(BDH) grade. The solutions were made in air-free doubly distilled conductivity water. Polarographic measurements versus SCE were carried out at 30°, 40° and 50°C (±1°) at $\mu = 2M$ in water, aq. DMF or aq. DMSO (20% v/v) with a manual type polarograph as described earlier. The d.m.e. had the following characteristics: $m = 2{\cdot}4$ mg/sec and $t = 2{\cdot}9$ sec.

The most suitable *p*H for the Cd(II)-TDAA system was 6·5 while for the Pb(II)-TDAA system it was 6·0. For the determination of stability constants for the Cd(II) system, the (ligand) was varied from 0·00-0·45*M* while in Pb(II) system (ligand) was varied from 0·0-0·2*M*. All calculations were done on the basis of the theories given by Lingane[3], DeFord and Hume[4] and as improved by Irving[5].

Stability constants in the case of Cd(II)-TDAA system were calculated by DeFord and Hume method, since the plot of $-\log C_x$ versus $-E_{1/2}$ was not linear while for Pb(II)-TDAA system, it was calculated by Lingane's method since the plot of $-\log C_x$ versus $-E_{1/2}$ was linear.

The number (*p*) of ligand/Pb ion were determined using the expression

$$p = -\frac{d(E_{1/2})_c}{d(E_{1/2})_s} \Big/ -\frac{RT}{0{\cdot}4343nF}$$